

Short Review

Graphene Supported Nanocomposite for Electrochemical Detection of Pollutant Materials: A short Review.

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The heavy metal ions and pollutant are considered as a one of the major problem in environmental contamination. Hence detection of trace level pollutant becomes a more research area in today. Graphene oxide nanocomposite is important in sensor research; it has special physical and chemical properties. Modified graphene oxide nanocomposite can be absorbing pollutant material ions in a high efficiency and selectivity. In this review focused on the Preparation of different type of graphene oxide nanocomposite and it characterized by different spectroscopy. Minimum number of graphene nanocomposite sensors with low limit of detection was reported to detect towards pollutant.

Keywords: Environmental Pollutant, Graphene oxide nano composite, Preparation, spectroscopy properties.

1. INTRODUCTION

The globulation and rising population has becomes the biggest environmental challenge. Environmental pollution especially toxic materials in air and water caused by human, industry and agricultural activities. The human body accumulate the pollutant materials form food cycle will cause dangerous disease; therefore it is more important to detection and removal from environmental [1-4]. Water as a major contamination source in the globe. Water pollution is the contamination of natural water like lakes, rivers, oceans, and ground water. These kinds of environmental pollution are directly or indirectly affected by human and living organisms. Here we mention this article Graphene oxide supported nanocomposite used for detection of environmental pollutant compounds. Hydrazine, phenol and Arsenic are the major water pollutant agents. Arsenic is naturally occurring element which is widely spread in earth. Arsenic exists in various allotropes although it is mainly used in industry. Arsenic and it derivatives are especially used in the manufacturing of pesticides, herbicide and insecticides. Millions of people affected across the world by arsenic contamination in ground water.

Arsenic derivatives are used in various agricultural insecticides and poisons. Inhalation of arsenic can cause a variety of disease such as dermal changes, gastrointestinal, respiratory, cardiovascular, genotoxic, mutagenic, and carcinogenic. The world health organization (WHO) arsenic guideline values for drinking water 10 PPb. Many methods are available for detection of arsenic. Even though electrochemical methods are most suitable for arsenic detection in cause time consuming, low-cost, accurate value and easy handling [5-16, 53-63]. Hydrazine is an inorganic compound it is dangerous unstable and unless, it is an alkali nature. In their pure form of hydrazine is clear, colorless liquids. These liquids can evaporate in air. Hydrazine smell like ammonia it is easily reacts and catches with fire. It is released directly to the air quickly destroyed by reactive molecules in air. Hydrazine and its derivatives have more application in agricultural, industrial, and defense. It also used as a starting material for many chemical reactions. It is a moderately toxic and harmful to human, animal and plants. It affects the liver, brain, DNA, blood normality, and nervous system, so the detection of hydrazine is more important today [17, 18]. Phenol is also known as aromatic organic compound it is highly reactive to other compound toward high electrophilic substitution and also easily formation of alkylation, halogenations and sulfonation. It is soluble in water so easily making contamination with water, it is also used as a precursor material for large collection of drug especially aspirin, pesticide, dyes, plastics, and explosives. This compound has significant toxic effect on human being, animal, and plant. Therefore Phenolic compound detection is more important one. [19-21, 53]. Currently nanotechnology used in various field like medicine, pharmaceuticals and environmental etc. This is the solution for environmental cleaning and improving [22]. Graphene oxide as a two dimensional, thickness carbon sheet, It has been more application in chemistry, physics, material science and biology. Graphene oxide as a unique material for nanotechnology, modified graphene [23, 24] materials has been used in solar cell research [25], lithium ion battery [26], super capacitors [27], catalysis [28] and environmental [29]. The graphene based sensor device for pollutant device [30]. Graphene oxide has a theoretical surface area of $2630 \text{ m}^2 \text{ g}^{-1}$ and also has highest mechanical, thermal and electrical properties. Currently graphene nanocomposite as a valuable materials and it can be used for various energy storage and sensor device. The graphene oxide nanocomposite has more active than graphene oxide; it is also used for detection and removal of heavy metal ions. [31]. In this review we discuss about the graphene nanocomposite and its towards Environmental pollutant detection.

2. PREPARATION OF MnO_2 -GRAPHENE OXIDE (MnO_2/GO) NANOCOMPOSITE FOR HYDRAZINE DETECTION

It is important and widely used method for preparation of graphene oxide by hummer method [33] and reduced by electrochemical and chemically. The metal nanoparticle decorated on the graphene oxide surface, then after modified graphene oxide nanocomposite for using detection of water pollutant. [34-41] lei et al. prepared more surface area $\text{MnO}_2/\text{graphene oxide}$ nano composite by sonication method. The prepared material was coated onto the GC surface, and obtained $\text{GC}/\text{MnO}_2/\text{GO}$; the prepared material used for detection [37] of hydrazine.

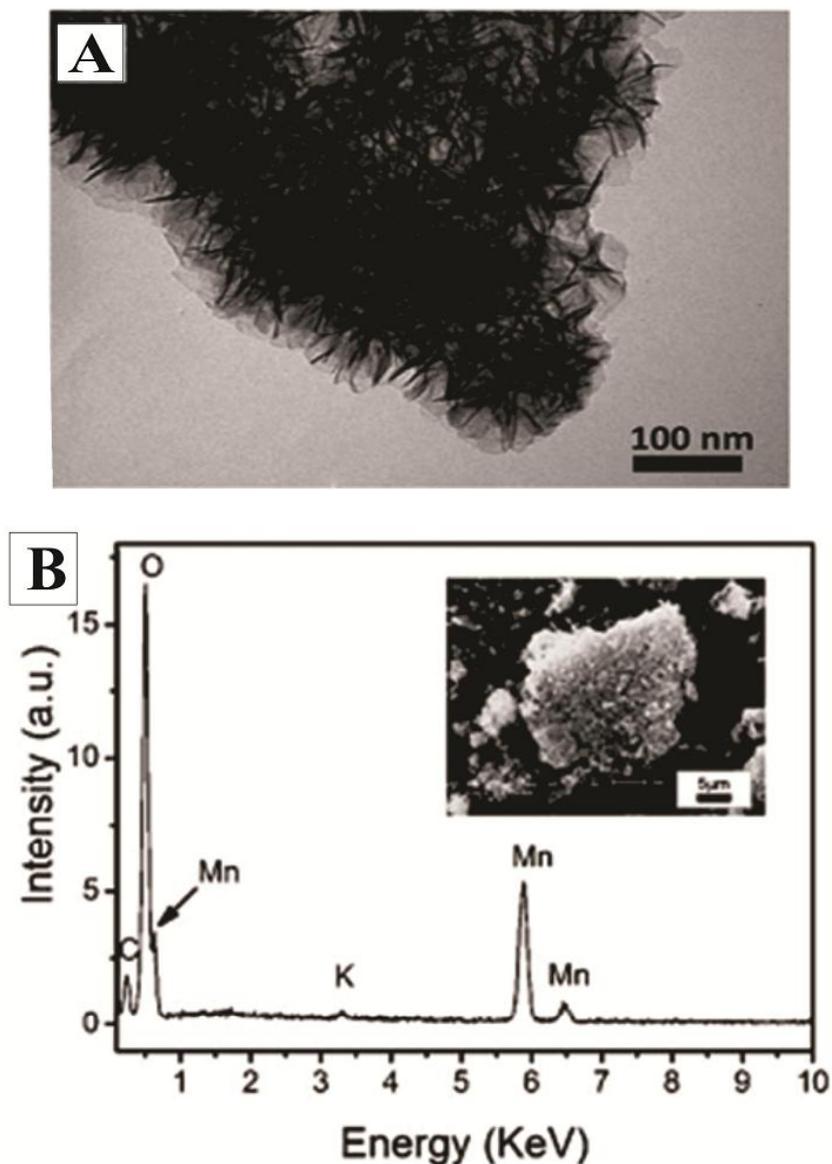
2.1 Characterization of MnO₂-graphene oxide (MnO₂/GO) Nanocomposite,

Figure 1. TEM image of GO/MnO₂ nanocomposite (A), EDX of GO/MnO₂ nano composite (B). [Reproduced with permission from reference 39]

A variety of technique has been used for the characterization of graphene oxide nanocomposite, such as Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-Ray diffraction (XRD), Atomic force microscopy (AFM), X-ray photo electron spectroscopy (XPS), Cyclic voltammetry (CV), UV-Vis, Raman, and FT-IR spectroscopy (Figure 1A), shows clearly a TEM image of graphene oxide Nanocomposite, It is found that synthesized graphene oxide as a smooth surface area after MnO₂ nanoparticle homogeneously dispersed on the Graphene sheet. The prepared nanocomposite is more stable and electrocatalytic activity towards hydrazine in case of more interaction between graphene oxide and MnO₂ nanoparticle, [64, 65] The EDX of GO/MnO₂ Nano composite, and the chemical composition of the GO/Mno₂ nanocomposite have been characterized by EDX. (Figure1B) The high magnification of TEM image, more detail about the morphology and

nanoparticle arrangement is observed. The MnO₂/GO Nanocomposite [39] is confirmed by FT-IR Spectra, the results show that several characteristic peak of GO and GO/MnO₂ Nanocomposite. The synthesized nanocomposite was characterized by XRD measurement, and also confirmed. The reflection explained MnO₂ nanoparticle formation as a face- centered-cubic Phase structure.

2.2 Detection of hydrazine by MnO₂-graphene oxide (MnO₂/GO) Nanocomposite,

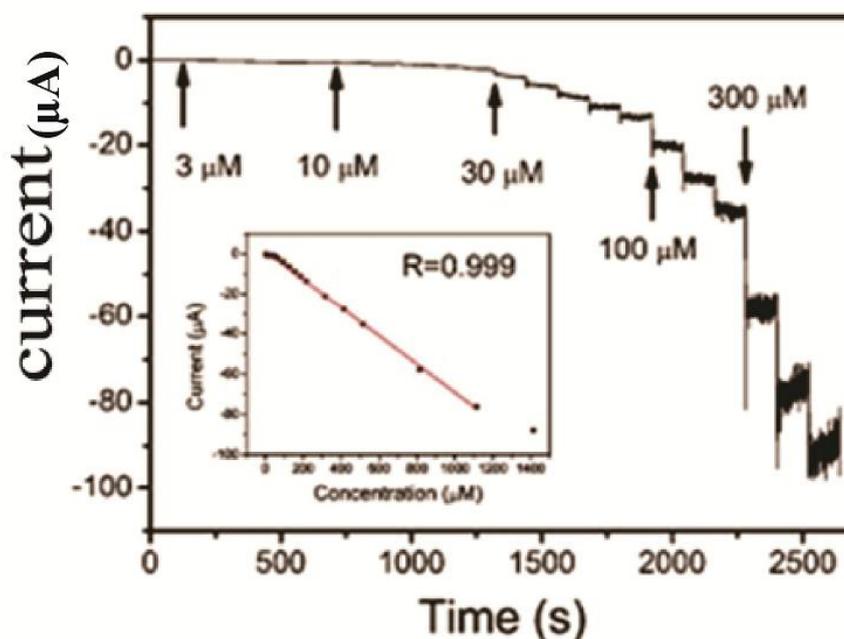
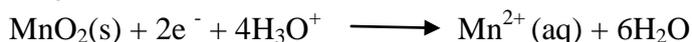


Figure 2. Amperometric response of the GO/MnO₂ nanocomposite. [Reproduced with permission from reference, 39]

Figure 2, shows the amperometric experiments were carried out at 0.6 V in pH 7 phosphate buffer solutions under continuous stirring. Increasing the hydrazine concentration the current also increasing. [39] The study state current has a linear relationship with the concentration of hydrazine range up to 1.12 mM with a coefficient of 0.999, the detection limit (LOD) 0.16µM and 1007 µAmM⁻¹cm⁻² respectively. So the detection limit of MnO₂/GO/GCE is excellent and also it is a good candidate for hydrazine detection with high performance. The MnO₂/GO/GC electrode showed good selectivity and stability as well as. The overall oxidation and reduction of Mn species (68, 39) shows below.



So the prepared Nanocomposite has great sensitivity, selectivity, stability and linear range,

3. PREPARATION OF Au - GRAPHENE OXIDE NANOCOMPOSITE (Au/GO) FOR PHENOLIC COMPOUND DETECTION,

Tang et al, Reported, Graphene oxide prepared from natural graphite based on modified hummer method. [42] The prepared graphite was dispersed in 0.067 M, pH 9.18 Phosphate buffer

solution. The AuNPs were electrodeposited on the RGO surface [66]. The modified (Au/RGO/GCE) the potential range -0.30v, for 250s. Prepared reduced graphene oxide-Au nanocomposite used for detection of 4-nitrophenol.

3.1 Characterization of Au-Graphene oxide (Au/GO) nanocomposite,

The morphological nature of Graphene oxide-Au nanocomposite was characterized by SEM image (Figure 3); 70nm size of the Au nanoparticle was deposited on the graphene oxide surface by coagulation, [42-45] the electrochemical active surface area of glassy carbon electrode increasing after the modification. And also increasing the conductivity of the (Au/GO) nanocomposite.

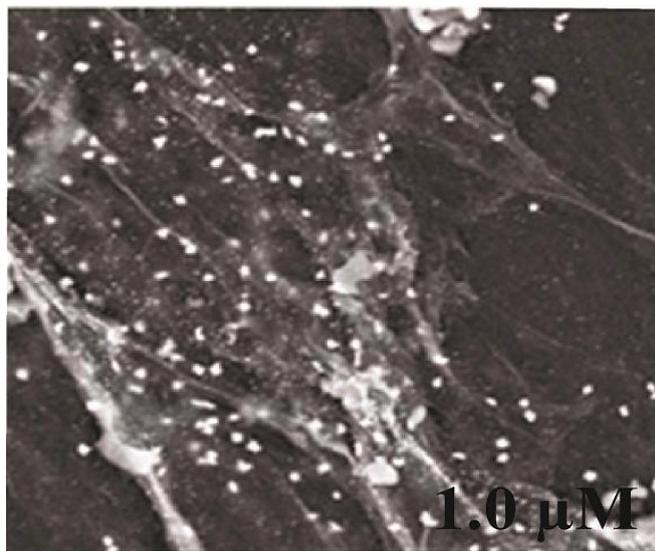
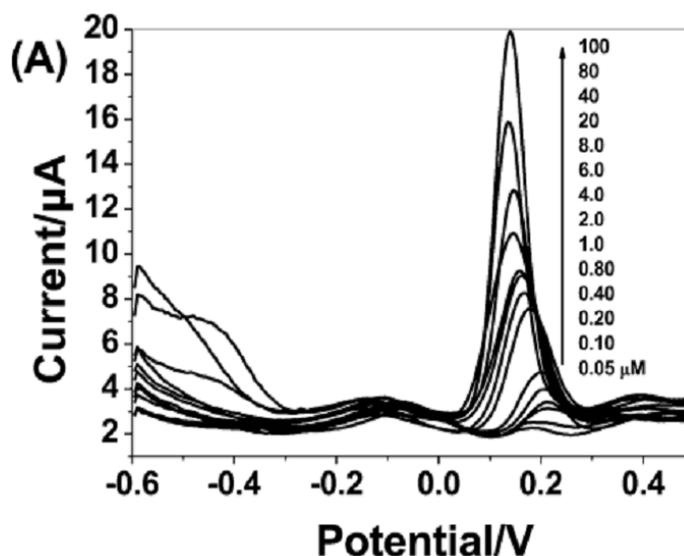


Figure 3. SEM image of reduced graphene oxide-Au nanocomposite [Reproduced with permission from reference 42]

3.2 Detection of Phenolic compound by Au-graphene oxide (Au/GO) nanocomposite,



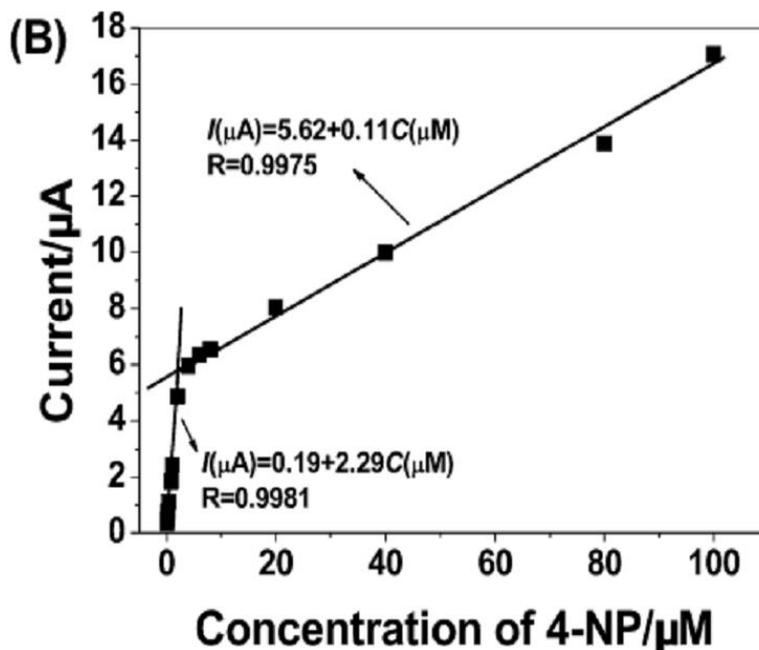


Figure 4. DPV curves (A); calibration plot of the DPV curves (B). [Reproduced with permission from reference 42]

Figure 4A shows, 4-Nitrophenol was individually detected by DPV method. The AuNPs/RGO composite modified electrode under the optimized condition. Each addition was measured for 3 times, obtaining 3 % standard deviation which indicate excellent reproducibility. Hence Oxidation and reduction of phenol as a main role for this sensor [67], The DPV curves show different concentration of 4-Nitrophenol obtained two linear concentration ranges (Figure 4B), 0.05-2.00 μm and 4.00-100 μm the limit of detection 0.01μm. It is mention that this if more efficient sensor than other, [42,66] The Graphene oxide AuNPs shows enhanced analytical performance, and also the sensing and stability. Therefore it is feasible electrochemical sensor for the Detection of 4-Nitrphenol.

4. PREPARATION OF SILVER- GRAPHENE OXIDE NANOCOMPOSITE (Ag/GO) FOR ARSENIC DETECTION

Dar et al, coworker's reported GO was synthesized from natural graphite by hummer method, generally metal nanoparticle preparation using strong reducing agent because it is more toxic to the environmental [41]. GO powder was dispersed in water by simple sonication and then 0.2 g β-Cyclodextrin and AgNO₃ was added, The colloidal suspension was stirred and then 10 ml of 2.6 % ascorbic acid was added finally the Ag/GO nanocomposite was formed. The obtained product was dried and used for electrode material as an arsenic detection. [43] Here this preparation using, ascorbic acid as the reducing agent and β-Cyclodextrin as the stabilization agent.

4.1 Characterization of Silver-Graphene oxide (AgNPs/GO) nanocomposite,

FT-IR Spectra shows Graphene-Pt nanocomposite, the graphene oxide appear strong and broad band at 3250 cm^{-1} due to $-\text{OH}$ stretching vibration. The carbonyl stretching frequency was observed at 1728 cm^{-1} , epoxides and hydroxide were observed at 1616 cm^{-1} . The stretching frequency of the aromatic ring was observed found to be 1387 cm^{-1} . The XRD pattern of (Figure 5 B). the graphene – Platinum nano particle confirm and also platinum particle on the graphene oxide surface [43]. The TEM image shows, Figure 5 A, the typical crumbled and wrinkled surface structure of graphene oxide, and also showed large surface area. The AgNPs completely and uniformly distributed on the Graphene oxide surface. [46-50] without any agglomeration.

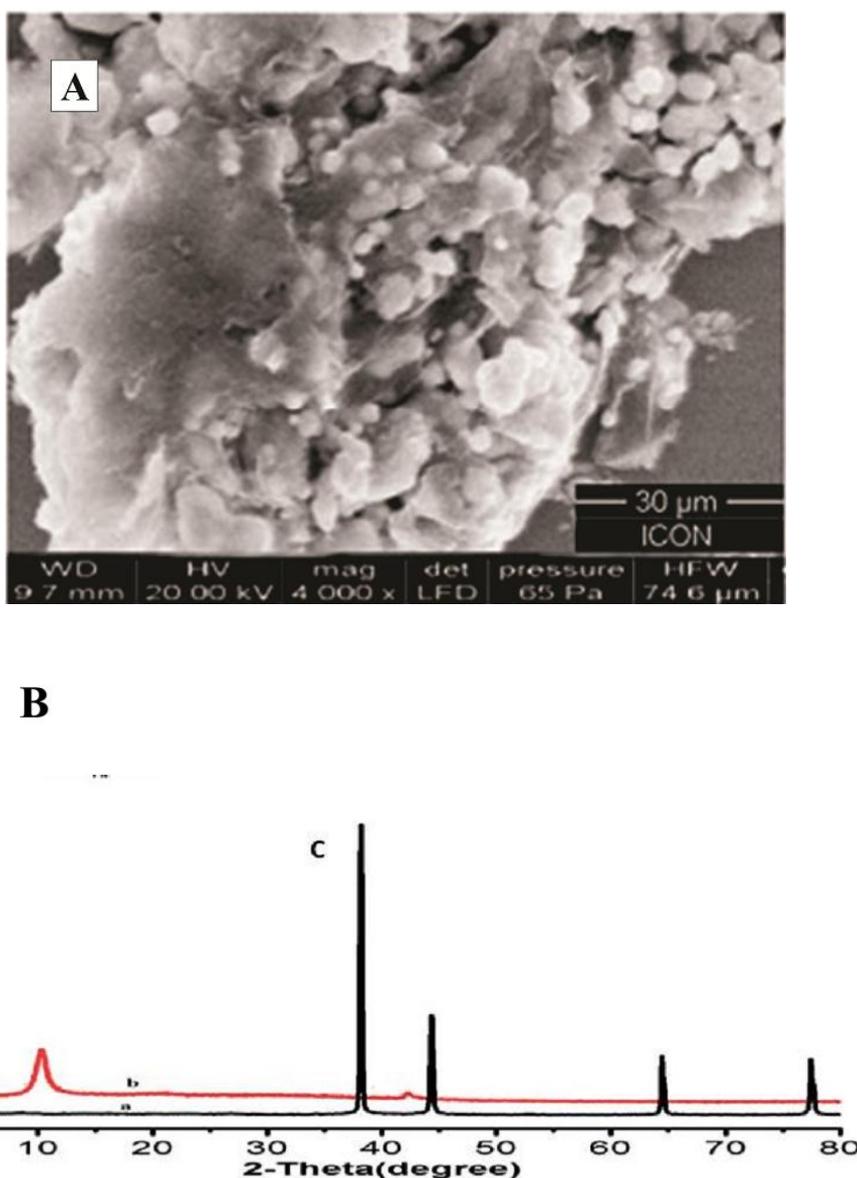


Figure 5 A. SEM image of AgNPs-Graphene oxide nano composite, B. XRD Spectrum of AgNPs-Graphene oxide nano composite, GO (a), AgNPs-Graphene oxide (b). [Reproduced with permission from reference, 43]

4.2 Electrochemical Detection of Arsenic by silver-Graphene oxide (Ag/GO) nanocomposite.

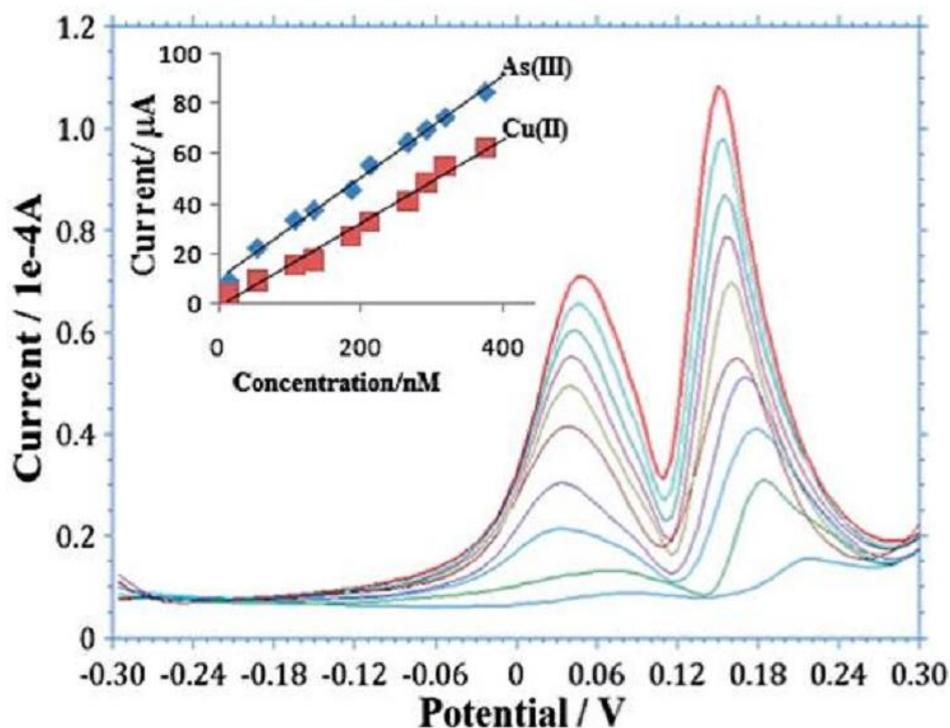


Figure 6. The simultaneously detection of arsenic at AgNPs/GO nanocomposite using by SW-ASV. [Reproduced with permission from reference, 43]

The detection performance was characterized by SW-ASV method. (Figure 6) The peak height also increased increasing the concentration of arsenic As (III) from 13.33 to 375 nM. The sensitivity and limit of detection of the prepared sensor estimated to be $180.5 \mu\text{m}^{-1}$ and 0.294 nM. The obtained data were compared with other modified electrode the limit of detection, sensitivity; linear calibration range and stability is better than other modified electrode. [43] In case graphene silver nano composite as an eminent electrode materials for arsenic sensor. Determination of Arsenic in natural water as a challenging task because other interfering materials also present with arsenic. AgNPs-GO/GC electrode using SW-ASV is shown appear well defined peak for arsenic detection [51, 52], it is observed from the figure there is no interfering materials. The result performance good reproducibility, stability, and also AgNPs/GO nanocomposite [69, 70] as a good sensor material for arsenic detection.

5. CONCLUSIONS

We have summarized the graphene oxide Nanocomposite prepared and has been used for Environmental pollutant and detection, Individual graphene oxide has not special properties but combine with metal nanoparticle, it has enhanced physical, and chemical properties, this review article mentioned some important graphene oxide Nanocomposite used as a sensor material. This composite material towards detection of environmental pollutant such as Hydrazine, Phenolic compound and Arsenic.

References,

1. A. Vaseashta, M. Vaclavikovic, S. Vaseashta, G. Galliosd, P. Royb, O. Pummakarnchana, *Science and Technology of Advanced Materials* 8 (2007) 47
2. S. Yunus, Harwin, A. Kurniawan, D. Adityawarman, A. Indarto *Environmental Technology Reviews* 1(2012)136
3. P. Bhawana, M.H. Fulekar, *Research Journal of Chemical Sciences*, 2 (2012) 90
4. Y.Weii, C.Gao, F.L.Meng, H.H.Li, L.Wang, J.H.Liu, X.J.Huang. *J. Phys. Chem. C* 116 (2012) 1034.
5. B. Guerini, S. I. M. Reddy, N. B. R. K. Venigobal, *Environmental pollution.*, 67(1990)97.
6. B. Sui, B. Kim, Y. Zhang, A. Frazer, K. D. Belfield. *ACS Appl Mater Interfaces.*, 5 (2013) 2920.
7. H. Aboubakr, H. Brisset, O. Siri, J. M. Raimundo, *Anal. Chem.*, 85 (2013) 9968.
8. W. Q. Lu, S. H. Xie, W. S. Zhou, S. H. Zhang, A. L. Liu. *Open Environmental Sciences.*, 2(2008)1.
9. J. Zhu, R. Sadu, S. Wei, D. H. Chen, N. Haldolaarachchige, Z. Luo, J. A. Gomes, D. P. Young, Z. Guo, *ECS Journal of Solid State Science and Technology.*, 1 (2012)1
10. J. A. G. Santos, M. I. S. Gonzaga, L. Q. Ma, M. Srivastava, *Environmental Pollution.*, 154 (2008) 306.
11. X. Dai, R. G. Compton, *Analyst*, 2006, 131, 516–521.
12. B. K. Mandal, K. T. Suzuki, *Talanta*, 2002, 58, 201.
13. WHO, Geneva, 1993 (<http://www.who.int/int-fs/en/fact210.html>)
14. X. C. Le, X. F. Lu, X. F. Li, *Anal. Chem.*, 76 (2004) 27.
15. D. Q. Hung, O. Nekrassova and R. G. Compton, *Talanta.*, 64 (2004) 269.
16. A. Cavicchioli, M. A. La-Scalea and I. G. R. Gutz, *Electroanalysis.*, 16 (2004) 697
17. E. Lee, D. Kim, J. M. You, S. K. Kim, M. Yun, S. Jeon, *Journal of Nanoscience and Nanotechnology.*, 12 (2012) 8886.,
18. M.R. Ganjali, F. Faridbod, N. Davarkhah, S.J. Shahtaheri, P. Norouzi., *Int. J. Environ. Res.*, 9(1) (2015) 333.
19. J. Liu, Y. Chen, Y. Guo, F. Yang, F. Cheng, *Journal of Nanomaterials* (2013) 6.
20. P. Gao, Y. Feng, Z. Zhang, J. Liu, N. Ren., *Environmental Pollution* 159 (2011) 2876.
21. W.Q. Lu, S. H. Xie, W. S. Zhou, S. H. Zhang, A. L. Liu, *Open Environmental Sciences.*, 2 (2008) 1.
22. P. Mehndiratta, A. Jain, S. Srivastava, N. Gupta, *Environment and Pollution*, 2 (2013)
23. G. Zhao, T. Wen, C. Chen, X. Wang, *RSC Advances*, 2 (2012) 9286
24. L.U.M.Jiao, L. I. Jing, Y. X. Yu, Z. C. An, Y. Jia, H. Hao, W. X. Bao *Chin Sci Bull* 58 (2013), 28.
25. J. Wu, M. Agrawal, H. A. Becerril, Z. Bao, Z. Liu, Y. Chen, P. Peumans, *ACS Nano*, 2010, 4, 43.
26. R. E. Sabzi1, F. Rasouli1, F. Kheiri, *American Journal of Analytical Chemistry.*, 4 (2013) 607.
27. Z. Chen, M. Zhou, Y. Cao, X. Ai, H. Yang and J. Liu, *Adv. Energy Mater.* (2) 2012 95.
28. D. W. Wang, F. Li, J. Zhao, W. Ren, Z. G. Chen, J. Tan, Z. S. Wu, I. Gentle, G. Q. Lu and H. M. Cheng, *ACS Nano* (3) 2009, 1745.
29. R. Kou, Y. Shao, D. Wang, M. H. Engelhard, J. H. Kwak, J. Wang, V. V. Viswanathan, C. Wang, Y. Lin and Y. Wang, *Electrochem. Commun.* 11 (2009) 954.
30. G. Zhao, L. Jiang, Y. He, J. Li, H. Dong, X. Wang and W. Hu, *Adv. Mater.* 23, 2011, 3959.
31. D. Zhao, G. Sheng, C. Chen and X. Wang, *Appl. Catal., B*, 111(2012) 303.
32. H. Chang., H. Wu, *Energy Environ. Sci.*, 6 (2013) 3483
33. J.R.W.S. Hummers, R. E. Offeman, Preparation of Graphitic Oxide *J. Am. Chem. Soc.*, 80 (1958), 1339
34. R. Ramachandran, V. Mani1, S.M. Chen, R. Saraswathi2, B. S. Lou3, *Int. J. Electrochem. Sci.*, 8 (2013) 11680
35. A. Krittayavathananon, P. Srimuk, S. Luanwuthi, M. Sawangphrukn., *Anal. Chem.* 86 (2014) 2272.
36. R. Devasenathipathy, V. Mani, S. M. Chen., *Talanta* 124 (2014) 43
37. S. E. Baghbamidi1, H. Beitollahi, S. Tajik. *Anal. Bioanal. Electrochem.*, 6 (2014) 634..
38. Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, *Adv. Mater.*, 2010, 1

39. J. Lei, X. Lu, W. Wang, X. Bian, Y. Xue, C. Wang, L. Lib, *RSC Adv.*, 2 (2012) 2541.
40. E. Lee, D. Kim, J. M. You, S. K. Kim, M. Yun, s. Jeon, *Journal of Nanoscience and Nanotechnology*,. 12 (2012) 8886.
41. Y. J. Yang, W. Li, X. Wu. *Electrochimica Acta.*, 123 (2014) 260–267.
42. Y.N.Tang, R. Huang, C. Liu, S. Yang, Z. Z.Lua, S. Luo, *Anal Methods*,. 5 (2013) 5508.
43. R. A. Dar, N. G. Khare, D. P. Cole, S. P. Karna, A. K. Srivastava, *RSC Adv.*, 4(2014)14432.
44. D. W. Wang, I. R. Gentle and G. Q. Lu, *Electrochem Commun.*, 10(2010), 1423.
45. D. K. Kampouris and C. E. Banks, *Chem. Commun.*, 47(2010), 8986
46. R. P. Gopalan, *Int. J. Nanosci.*, 9(2010)487.
47. B. D. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley Company, USA, 1956
48. J. Rita and S. S. Florence, *Chalcogenide Lett.*, 6(2009)269.
49. Y. Sun and Y. Xia, *Science*, 298 (2002) 2176.
50. D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, *Nature*,. 448 (2007) 457.
51. A. O. Simm, C. E. Banks , R. G. Compton, *Electroanalysis*, 17(2005) 1727.
52. R. Feeney , S. P. Kounaves, *Anal. Chem.*, 72(2000) 2222.
53. I. C. McCalla, A. Betanzosb, D. A. Weberb, P. Navab, G. W.Millera, C. A. Parkosb, *Toxicol Appl Pharmacol.*, 241 (2010) 61.
54. P. S. Virosta, S. Espín, A.J. G. Fernández , T. Eeva, *Science of the Total Environment*, 512 (2015) 506.
55. M.F. Hughes, B. C. Edwards, K.M. H.Davis, J. Saunders, M. Styblo, D. J. Thomas, *Toxicology and Applied Pharmacology*,. 249 (2010) 217.
56. C.H.Syu, C.C.Huang, P.Y.Jiang, C.H.Lee, D.Y.Lee, *Journal of Hazardous Materials.*, 286 (2015) 179.
57. A. A. Duker, E.J.M. Carranza, M. Hale, *Environment International*. 31 (2005) 631.
58. M. Subhani, I. Mustafa, A. Alamdar, I. A. Katsoyiannis, N. Ali, Q. Huang , S. Peng , H. Shen, S. A. M. A. S.Eqani, *Ecotoxicology and Environmental Safety*,. 115 (2015) 187.
59. P.G.Rubio, J.Roberge, L. Arendell, R. B. Harris, M. K. ORourke, Z. Chen, E. C. Soto, M.M. M. Montenegro, D. Billheimer, Z. Lu, Walter T. Klimecki, *Toxicology and Applied Pharmacology*,.252 (2011) 176.
60. J. An, J. Lee, G.Lee, K.Nam, H. O. Yoon, *Micro chemical Journal*, 120 (2015) 77.
61. T. Leveque, Y. Capowiez, E. Schreck, S. Mombo, C. Mazzia, Y. Foucault, C. Dumat, *Science of the Total Environment*,. 511 (2015) 738.
62. Y. Lu, S. Song, R.Wang, Z.Liu, J.Meng, A.J. Sweetman, A.Jenkins, R.C. Ferrier, H.Li, W.Luo, T.Wang, *Environment International*,. 77 (2015) 5.
63. F.G.Huang, S.Y.Jia, Y. Liu, S. H. Wu, X. Han, *Journal of Hazardous Materials*, 286 (2015) 291
64. M. Wang, C. Wang, G. Wang, W. Zhang and F. Bin, *Electroanalysis*, 22 (2010)1123.
65. J. J. Xu, X. L. Luo, Y. Du and H. Y. Chen, *Electrochem. Commun.* 69 (2004)1169.
66. J. M. Gong, T. Zhou, D. D. Song and L. Z. Zhang, *Sens.Actuators, B*, 150 (2010) 491.
67. K. C. Honeychurch and J. P. Hart, *Electroanalysis*19 (2007) 2176.
68. E.R. Stobbe, B.A. de Boer, J.W. Geus *Catalysis Today* 47 (1999) 161.
69. S. Vijay Kumar, N.M. Huang, H.N. Lim, A.R. Marlinda, I. Harrison, C.H. Chia, *Chemical Engineering Journal* 219 (2013) 217.
70. K. Z. Kamali, A. Pandikumar, G. Sivaraman, H.N.Lim, S. P. Wren, T. Sund, N. M. Huang, *RSC Adv.*, 2015, 5, 17809.